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Interaction of Perchloroethylene with Cerium Oxide in Three-Way Catalysts

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Abstract

The role of cerium oxide on direct oxidation of perchloroethylene (PCE) by a three-way catalyst was explored. In the absence of an external oxidizing agent, PCE was oxidized over an alumina supported Pt/Rh three-way catalyst. We hypothesize that the chlorine atoms in the adsorbed PCE interact with oxygen in CeO₂, reducing the cerium to create CeCl₃.

Keywords

Perchloroethylene; Cerium oxide; Reactive adsorption; Three-way catalyst

1 Introduction

Reactive adsorption of chlorinated hydrocarbons (CH₂Cl₂, CHCl₃, CCl₄) on CaO was explored by Koper et al. [1], who demonstrated that CCl₄ reacts with the surface to form CaCl₂ and CO₂. Weckhuysen et al. [2] extended this work to the reaction of CCl₄ with alkaline earth metal oxides as a group. They observed the formation of an oxygenated intermediate, COCl₂. Lanthanum and cerium oxides proved effective at removing CCl₄, with cerium oxides showing complete conversion to CeCl₃ at temperatures above 450 °C [3]. They proposed the following overall reaction

Van der Avert et al. [4] reported that the presence of steam promotes the conversion of CCl₄ on lanthanum and alkaline earth metal oxides, preventing destruction of the oxides and creating a catalytic effect [5]. The mechanistic implications and relative activities of intermediates from the CCl₄ reaction with lanthanum oxides also have been explored [6,7].

Commercial three-way catalysts (TWC) used in automobile catalytic converters consist of an inert support, a wash coat and the noble metal catalysts. The cordierite support often has a honeycomb structure that is covered in a wash coat containing alumina, cerium, zirconium and other trace constituents. The wash coat is used to deposit noble metals (Pt, Rh, or Pd) in a dispersed fashion. Cerium oxide is used to create a more stable wash coat with a larger dispersion of noble metals [8,9]. Cerium also increases both the thermal resistance [10] and the oxygen storage capacity [11] of the TWC. In recent years, cerium zirconium oxides

($\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$) have begun to replace cerium oxide due to greater oxygen storage capacity and improved thermal properties [12]. Oxygen mobility is increased in cerium and zirconium oxides [13,14]. In an oxidizing environment, the cerium oxide exists as CeO_2 , while the reduced form is Ce_2O_3 .

Bedrane et al. [15] noted that the oxygen storage capacity of cerium oxides depends on both the metals present and the surface temperature. In general, higher temperatures produce higher capacities. Oxygen storage capacity proved to be greater with platinum present than with rhodium. Studies were not done with both metals present, but all metals increased oxygen storage capacity over non-metallic baselines. The oxygen storage capacities of cerium zirconium oxides were more sensitive to temperature than were similar wash coats without Zr. It was also noted that storage capacity plateaux existed above 450 °C. Attempts to model and quantify this phenomena have been reported [16].

Interactions of oxygen with the catalyst are particularly important in catalyzed oxidative dehalogenation of chlorinated organics. Detailed kinetics of catalytic oxidation may follow either a Langmuir–Hinshelwood type of mechanism (reaction between adsorbed oxygen and an adsorbed reactant) or an Eley–Rideal mechanism (reaction between adsorbed oxygen and a gas-phase reactant molecule), which may lead to a complete mineralization of the chlorinated hydrocarbon to CO_2 , producing HCl and, in some cases, Cl_2 [17–20]. A disadvantage of oxidation of chlorinated hydrocarbons is the requirement of relatively high temperatures to achieve an efficient process and inhibit the formation of toxic by-products, such as dioxins and furans. On the other hand, reductive dehalogenation in the presence of a hydrogen source occurs at lower temperatures but leads to catalyst deactivation [21]. Recently, we have shown that deactivation can be prevented by performing the catalytic reductive dehalogenation of PCE in the presence of oxygen on a TWC [22], indicating that oxygen availability and mobility on the catalytic surface plays an important role in this process. Our experiments showed that PCE could be destroyed on the TWC even in the absence of oxygen or a hydrogen source in the feed to a continuous reactor. Here, we report on the reactive adsorption of PCE on a TWC. The cerium zirconium oxide present in the TWC acts to remove chlorine from PCE to create a chlorinated surface and carbon dioxide. The reaction occurs at temperatures above 450 °C and eventually consumes the stored oxygen. The reaction can be extended and the surface can be recovered by adding water vapor to the influent gas stream.

2 Experimental

2.1 Catalyst

Catalyst monoliths (2.54 cm OD $\times$ 2.54 cm length cylinder) were cut from a commercially available 820 cm^3 catalyst honeycomb block. The Pt/Rh ratio was 3:1 wt/wt, deposited on a support comprised of cordierite (90%) and a wash coat (10%) containing alumina, cerium zirconium oxide, and other trace constituents. The monolith contained 0.185 mg total noble metal/ cm^3 with a honeycomb cell density of 62 cells/ cm^2 . Each cell had a cross Sect. 1 mm $\times$ 1 mm. The catalyst solid and void volumes were 12.87 and 9.36 cm^3 , respectively. The void volume was determined by immersion of a blank monolith in heptane. The commercially available (Applied Ceramics, Inc., Doraville, Georgia) unamended alumina support exhibited no PCE conversion when PCE and N_2 were passed through the support at temperatures up to 450 °C.

A scanning electron microscope image of the catalyst surface is shown in Fig. 1. Elemental analysis was performed via energy dispersive spectroscopy (EDS) at an accelerating voltage of 15.0 kV. The EDS spectra for points 1 and 2 in Fig. 1 are provided in Fig. 2a, b. The analysis indicates that the dark areas in Fig. 1 are alumina, and light areas are the cerium

zirconium oxide wash coat. Platinum and rhodium particles are present on both the cerium zirconium oxide and the alumina. It is evident that the wash coat is uniformly distributed over the cordierite surface. Particle sizes are broadly distributed with larger particles reaching a few microns in size.

2.2 Reactor System

Experiments were carried out in a 50 cm (long) by 2.54 cm (inner diameter) quartz tube (ACE Glassware), containing the 2.54 cm $\times$ 2.54 cm cylindrical catalyst monolith. The reactor was housed in a single-zone, temperature controlled tube furnace (Thermolyne 21100), aligned at a 45 ° angle to prevent possible accumulation of condensed products during reactor start up and shut down. The length of the furnace was 38 cm. The honeycomb was located inside the reactor tube, ~20 cm from the upstream end of the furnace. This allowed the gas to reach the furnace temperature before entering the honeycomb structure. Temperature was measured in two places using thermocouples: a K-type thermocouple (Omega Engineering) was placed at the center of the inlet face of the honeycomb (directly in contact with the solid surface of the honeycomb), and a Type Platinel II thermocouple was located at the furnace inner wall above the honeycomb (set point for temperature control). The gas temperature at the entrance of the honeycomb block was approximately equal to the furnace temperature at the operating conditions employed in this work.

Before each experiment, the catalyst was pretreated with a gas stream consisting of 5% O₂ and 95% N₂ overnight (12–16 h) at 500 °C. This was done in order to fully oxidize the surface to Ce_xZr_{1-x}O₂. Experiments were typically performed until conversion of PCE approached zero, an indication that available oxygen in the catalyst was fully consumed. Oxygen (99.9%, Air Liquide) and nitrogen (99.99%, The University of Arizona Cryogenics & Gas Facility) were used as obtained. Flows were regulated using needle valves (Swagelok) and mass control sensors (Omega Engineering, Inc.). Liquid PCE (Aldrich, 99.9+%) was placed in a modified flask located in an insulated water bath (20 °C). Nitrogen was passed over the surface of the PCE, entraining the vapor phase, which was then mixed with O₂ and N₂ at experiment-dependent ratios. The total flow rate was 0.5 L/min at room temperature, and concentrations of PCE were <600 ppmv. Residence times in the reactor ranged from 0.6 (catalyst at room temperature) to <0.2 s (catalyst at 400 °C and above).

2.3 Analytical

An HP 5890 gas chromatograph equipped with a flame ionization detector (FID) was used to analyze the influent and effluent streams. Gas samples were injected into the GC using Hamilton gas-tight syringes. A 0.53-mm wide-bore capillary column (J&W DB-624, 30 m $\times$ 0.53 mm $\times$ 3.0 mm) was used to separate hydrocarbons and chlorinated hydrocarbons. The temperatures of the injector and the detector were typically 200 and 250 °C, respectively.

2.4 Experiments

The catalyst temperature was adjusted to 100 °C under N₂-only conditions to begin a typical experiment. At that point, PCE was added into the system, and the temperature was gradually ramped up across the temperature range of the experiment. Inlet and outlet concentrations of PCE were measured every 20–25 °C. After every experiment, unless otherwise noted, the catalyst was regenerated for 12–16 h under 5% O₂ in N₂ (1 L/min) at 500 °C. Conversion of PCE was calculated from

$$X(\%) = \frac{C_{\text{PCE,in}} - C_{\text{PCE,out}}}{C_{\text{PCE,in}}} \times 100 \quad (2)$$

where $C_{\text{PCE,in}}$ and $C_{\text{PCE,out}}$ are the inlet and outlet concentrations of PCE, respectively.

3 Results and Discussion

3.1 Reactive Adsorption of PCE—Temperature Dependence

Reactive adsorption was indicated by differences in the inlet and outlet concentrations of PCE in N_2 at catalyst temperatures from 150 to 500 °C (Fig. 3). Control experiments without catalyst present or with only the alumina support produced no PCE conversion. In the presence of the TWC, PCE conversion began at a catalyst surface temperature of 350 °C and reached 100% at 400 °C. Weckhuysen et al. [3] reported that CCl_4 conversion began at 450 °C on high purity CeO_2 . In that work, the CeO_2 was pre-treated with oxygen at 600 °C overnight and exposed to pulses of CCl_4 while being monitored with in situ Raman spectroscopy. Results showed that cerium was reduced from Ce(IV) to Ce(III).

An experiment was run at 450 °C until PCE conversion was exhausted (Fig. 4). At this point, the inlet PCE source was removed, and the furnace was shut off. PCE desorption was not observed even at temperatures approaching 100 °C, indicating that the PCE removal mechanism is not simple adsorption on the monolith. This evidence, coupled with the lack of any detectable partially chlorinated byproduct, indicates that the PCE is indeed destroyed and may be completely converted to CO_2 . In the absence of an external oxygen source, the only oxygen present is in the form of cerium oxide, CeO_2 .

Similar to the mechanism proposed for CCl_4 destruction by Weckhuysen et al. [2], an overall (unbalanced) reaction for the reactive adsorption of PCE is

This is clearly not a catalytic reaction since it involves an irreversible change of the catalytic surface. Our inability to write a balanced reaction suggests that an intermediate such as CeOCl is likely to be present. It is known that crystals of CeOCl can be formed from CeO_2 under reducing conditions, and this material decomposes slowly at room temperature with only a partial loss of chlorine [23,24]. A chlorinated metal intermediate was also noted during CCl_4 conversion on alkaline earth metal oxides and lanthanum oxides [2,4].

A post-reactive adsorption (a similar experiment was performed to that described in Fig. 4) SEM image is shown in Fig. 5. The presence of chlorinated surface species is indicated through EDS performed on the sample shown in Fig. 5. The EDS spectra related to the SEM image in Fig. 5 is seen in Fig. 6. Point 1 in Fig. 5 (EDS scan shown in Fig. 6a) shows an increase in chlorine count in the cerium zirconium oxide from Fig. 2a, in which chlorine did not appear. Figure 6b, representing Point 2 in Fig. 5, with only a slight chlorine count indicates that the majority of chlorine is present in the cerium zirconium oxide.

3.2 Reactive Adsorption in the Presence of Other Reactants

In all experiments discussed to this point, the influent gas stream contained only PCE and N_2 . Other possible reactants of interest are water vapor and O_2 . Water is of particular interest, since it was previously shown that water both promotes the conversion of CCl_4 and regenerates the oxide [4].

Figure 7 shows the removal of PCE in the absence of other reactants, in the presence of water vapor and in the presence of oxygen. Water does not have an obvious positive effect on the conversion of PCE under these experimental conditions, but there is also no obvious negative effect. Oxygen, on the other hand, inhibited reactive adsorption. It should be noted

that the concentration of O₂ (4.5%) was much higher than the concentration of water vapor (0.5%) due to experimental restrictions. The temperature dependent data, with and without O₂, are similar to the data presented by Orbay et al. [22] for oxidation of PCE on the same catalyst material. It was suggested previously that oxygen competes with PCE and other chlorinated hydrocarbons for surface sites on the TWC and similar catalysts [22,25]. These results indicate that reactive adsorption occurs only in the absence of gas phase oxygen; the mechanism for this reaction is more complex than the direct oxidation of PCE by molecular oxygen sorbed on the catalytic surface.

One of the leading causes of catalyst deactivation during catalytic oxidation is chlorine poisoning. EDS performed on a catalyst that has undergone long term studies of catalytic deactivation indicates that chlorine is dispersed throughout the wash coat, present on both the alumina and cerium zirconium oxide. As noted in the discussion of Fig. 6, when the PCE removal process is reactive adsorption, chlorine is found almost exclusively on the cerium zirconium oxide, again indicating fundamental differences between the mechanisms of catalytic oxidation by O₂ and reactive adsorption.

3.3 Regeneration of Cerium Oxide

The reactive adsorption process results in the reduction of the cerium, as well as the replacement of lattice oxygen atoms with chlorine atoms. Were the reaction proposed in Eq. 3 fundamentally correct, the process would quickly consume the available cerium oxide. Previous work on lanthanum oxide showed that water vapor allows the reactive adsorption process to continue indefinitely [4], presumably by re-oxidizing the lanthanum oxide. In our experiments, however, 0.5% water vapor had little or no effect on PCE conversion (Fig. 8), PCE conversion gradually decreased, although conversion leveled off at 10% instead of degenerating to 0%.

4 Conclusions

The cerium zirconium oxide that is used to store oxygen in typical TWC applications also plays a role in the reactive adsorption of PCE. At temperatures above 400 °C, PCE is converted to carbon dioxide and cerium is reduced. The initially high conversion (>95%) is only momentary, as conversion drops to 10% within the first hour. EDS performed on the catalyst indicates the increased presence of chlorine on the cerium zirconium oxide.

Water vapor had little or no effect on the reactive adsorption process. The presence of oxygen in the reactor gas stream inhibits reactive adsorption, leading instead to catalytic oxidation at sufficiently high temperatures. Common use of a TWC will likely include the presence of O₂ in the influent gas flow, indicating that practical applications of the reactive adsorption process will be limited. To our knowledge, this is the first observation of reactive adsorption of a chlorinated C2 alkene, however, and applications may exist on pure cerium oxide, under certain conditions.

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Fig. 1. SEM image of three-way catalyst surface. *Point 1* is *centered* on cerium zirconium oxide, which is part of the wash coat. *Point 2* is *centered* on alumina, which occurs in both the wash coat and the support

Fig. 2.

a EDS spectra of *point 1* from Fig. 1. Large counts for both cerium and zirconium indicated that the light portion of the SEM image represents cerium zirconium oxide. **b** EDS spectra of *point 2* from Fig. 1. Presence of high counts of aluminum and virtual absence of other elements indicate that the dark portion of the SEM image is primarily alumina

Fig. 3.

PCE conversion as a function of catalyst surface temperature. Influent PCE concentration was 500 ppmv, and gas flow rate ($N_2 + PCE$) was 0.5 L min^{-1} at 25°C . PCE removal occurs only when the three-way catalyst is present and $T \geq 350^\circ\text{C}$. Legend: (◆) No catalyst present; (□) Unamended alumina support; (▲) Three-way catalyst

Fig. 4.

PCE concentration and catalyst surface temperature as a function of experimental run time. Influent PCE concentration was 700 ppmv. Gas flow rate of 0.5 L min^{-1} at 25°C . Conversion of PCE gradually decreases to zero over the initial 75 min. The furnace is turned off and the PCE source is removed at this point (indicated by *solid vertical line*) and no desorption of PCE is observed. At 130 min, the furnace is turned back on (indicated by *dashed vertical line*) and PCE desorption is still not observed. Legend: (◆) PCE inlet concentration; (□) PCE outlet concentration; (▲) Catalyst surface temperature

Fig. 5. SEM image of three-way catalyst surface after a reactive adsorption experiment. *Point 1* is centered on cerium zirconium oxide, which is part of the wash coat. *Point 2* is centered on alumina, which occurs in both the wash coat and the support. There is no readily visible difference between this image and the image shown in Fig. 1

Fig. 6.

a EDS spectra of *point 1* from Fig. 5. Large counts of both cerium and zirconium indicate the *light portion* of the SEM image depict cerium zirconium oxide. As compared to Fig. 2a, a large increase in chlorine count indicates the presence of a chlorinated species in the cerium zirconium oxide. **b** EDS spectra of *point 2* from Fig. 5. Presence of high counts of aluminum and little of other elements indicate *dark portion* of the SEM image depicts alumina. The lack of a large chlorine count indicates that chlorine is present primarily in the cerium zirconium oxide

Fig. 7.

PCE conversion as a function of catalyst surface temperature. Influent PCE concentration was 700 ppmv. Gas flow rate of 0.5 L min⁻¹ at 25 °C. Reactive adsorption occurs in the presence of H₂O, which does not have a promotion effect on the reaction. The presence of oxygen prevents reactive adsorption and instead creates catalytic oxidation. Legend: (◆) PCE only; (□) PCE and 0.5% H₂O; (▲) PCE and 4.5% O₂

Fig. 8.

PCE conversion as a function of experimental run time. Influent PCE concentration was 500 ppmv. Catalyst surface temperature was 475 °C. Gas flow rate of 0.5 L min⁻¹ at 25 °C. H₂O concentration of 0.5%. Conversion of PCE gradually decreases to 10% over 75 min. The presence of H₂O in the influent gas stream has no appreciable effect on the conversion of PCE